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PROCESS FOR THE PRODUCTION OF PROPYLENE FROM OLEFINIC STREAMS

The present invention relates to a process for the 10 production of propylene from prevalently olefinic hydrocarbon streams.

More specifically, the present invention relates to a selective cracking process for the production of propylene starting from mixtures of hydrocarbons, prevalently olefins, the above hydrocarbons having a boiling point ranging 15 from -15°C to +80°C, preferably from -12°C to +60°C.

A typical example of these fractions are essentially C₄-C₆ fractions coming from steam cracking and catalytic cracking, having an olefin content of at least 40% by 20 weight, usually at least 70% by weight.

Propylene is one of the most important chemical products from the point of view of demand and production volume and is mainly used in the production of polymers. The main propylene source is the steam cracking process, in which 25 hydrocarbon charges with a high paraffin content are ther-

mally treated in the presence of vapour. The main products of steam cracking are propylene and ethylene, which leave the process in a ratio of about 0.5. As the market request for propylene has become greater in the last few years with respect to that of ethylene and owing to the fact that the propylene/ethylene ratio cannot be significantly varied, it has become necessary to increase the production of propylene using alternative methods. In fact, in 1999 there was a considerable deficit of propylene in Western Europe, with importations of this product amounting to 195,000 tons. The production of large quantities of propylene by means of processes which appropriately treat steam cracking by-products can allow variations in the overall propylene/ethylene ratio, thus meeting market demands. The possibility of having flexible processes allowing a certain flexibility in the propylene/ethylene ratio would therefore provide great economic advantages.

An interesting possibility consists in a selective catalytic cracking process which converts C₄-C₅ fractions to propylene. The fractions can derive from steam cracking but it is also possible to extend the process to other similar streams coming for example from FCC (Fluid Catalytic Cracking). The charges can also derive from the above fractions after extraction and/or enrichment in olefins.

25 The use of solid acid catalysts, among which amorphous

silico-aluminas and in particular zeolites, in the cracking reaction of hydrocarbons, is known in literature (see for example J. Scherzer, Cata. Rev. - Sci. Eng., 31(3), 215-354, 1989).

5 The most important application of these materials in cracking reactions, from an industrial point of view, is that called FCC (Fluid Catalytic Cracking) whose purpose, starting from heavy charges such as vacuum gas oils, is to produce lighter hydrocarbon cuts, particularly within the
10 boiling range of gasolines. The catalysts currently used in this process are Y-type zeolites (IUPAC abbreviation: FAU) containing various additives.

A different type of cracking, owing to the charges used and type of products to be obtained, is called "selective cracking". The purpose of "selective cracking" is to produce light olefins, such as ethylene and propylene, starting from C₄-C₆ hydrocarbon fractions and therefore already light, if compared to a vacuum gas oil. The advantage of this process consists in transforming low quality hydrocarbon fractions, difficult to distribute on the market, to olefins having a higher added value.
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Various zeolitic materials active in "selective cracking" reactions, are described in literature. For example, EP-A-109,059 and EP-A-109,060 describe the use of ZSM-5
25 zeolite (IUPAC abbreviation: MFI) for selective cracking

reactions. These documents demonstrate that the best catalytic performances, referring to yields to propylene and ethylene, are obtained when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolite is high. More specifically, EP-A-109,059 claims, for 5 MFI-type zeolites (ZSM-5) $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios lower than or equal to 300 (mol/mol), preferably between 25 and 220, whereas EP-A-109,060 discloses $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios higher than or equal to 350 (mol/mol).

WO 99/57226 describes a method for converting hydro-10 carbon charges, with a boiling point within the naphtha range, to propylene in the presence of medium-pore zeolites having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio greater than 200 (mol/mol). The above document provides two experimental examples: in the first, three medium-pore zeolites ZSM-48 ($\text{SiO}_2/\text{Al}_2\text{O}_3 > 1500$), ZSM-22 ($\text{SiO}_2/\text{Al}_2\text{O}_3 > 1500$) and ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 55$) 15 are compared. It is shown that the selectivity to propylene for the first two catalysts is higher with respect to ZSM-5. In the second example, two ZSM-22 zeolites having a different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (>1500 and 120) are compared. It is 20 shown that the one with the greater $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio has the higher selectivity to propylene.

Finally, WO 99/29805 describes a process for producing propylene starting from C_4 and higher olefinic streams, in the presence of MFI zeolite (ZSM-5) having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ 25 ratio of at least 180 (mol/mol).

Experts in the field, however, still feel the necessity for using materials suitable for obtaining greater conversions and at the same time having a higher stability of the catalytic activity over a period of time. An extremely important problem, in fact, which is not taken much into consideration in literature, consists in the poor stability of the catalytic material over a period of time.

5 A process has now been found, which uses materials capable of improving the yield to propylene and that also have the great advantage of maintaining the catalytic performances practically constant over a period of time.

In accordance with this, the present invention relates to a process for the production of propylene starting from mixtures of hydrocarbons, prevalently olefins, the above 10 hydrocarbons having a boiling point ranging from -15°C to +80°C, preferably from -12°C to +60°C, which comprises putting the above mixture of hydrocarbons in contact, under cracking conditions, with a large-pore zeolite having a molar ratio Silica/Alumina lower than 200, preferably ranging 15 from 50 to 150.

The hydrocarbon mixtures essentially consist of hydrocarbons, both olefins and paraffins, having a boiling point ranging from -15°C to +80°C, preferably from -12°C to +60°C. Typical examples of hydrocarbons forming the above 20 hydrocarbon mixtures are 1-butene, trans-2-butene, cis-2-

butene, n-butane, isobutane, propane, pentane, isopentane, 1-pentene, 2-pentene, n-hexane, 1-hexene, 2-hexene. The hydrocarbon mixtures comprise from 30% to 100% by weight of olefins, preferably from 40% to 85% by weight. The paraffins contained in the hydrocarbon mixtures range from 5% to 65% by weight, preferably from 10% to 50% by weight, even more preferably from 20% to 45% by weight.

The term "cracking conditions" refers to a temperature at which the contact between the hydrocarbon mixtures and catalyst takes place, ranging from 400°C to 750°C, preferably from 450°C to 700°C, even more preferably from 500°C to 650°C.

The process of the present invention is preferably carried out at a weight hourly space velocity (WHSV) ranging from 0.1 h⁻¹ to 1,000 h⁻¹, more preferably from 0.5 h⁻¹ to 100 h⁻¹, even more preferably from 0.8 h⁻¹ to 50 h⁻¹.

The pressure in the contact zone between catalyst and hydrocarbon mixtures ranges from 0.1 to 30 absolute atm., preferably from 1 to 3 absolute atm., more preferably about 20 1 absolute atm.

The process of the present invention can be carried out using any reactor solution, for example, fixed bed, moving bed, a "riser" reactor or a fluid bed, preferably fixed bed.

25 The catalyst which can be used in the process of the

present invention is a large-pore zeolite having a molar ratio Silica/Alumina lower than 200, preferably ranging from 50 to 150. The term "large-pore zeolite" refers (see N.Y. Chen and T.F. Degnan, Chemical Engineering Progress, 5 February 1988, 32-41) to a zeolite have a lattice consisting of 12 tetrahedrons. The above zeolite has a molar ratio Silica/Alumina lower than 200, preferably ranging from 50 to 150. In the preferred embodiment, the zeolite is ZSM-12 (IUPAC abbreviation: MTW), having a molar ratio Silica/Alumina lower than 200, preferably ranging from 50 to 10 150. The preparation of this zeolite is well known to experts in the field.

The zeolite can be used as such or mixed with inert products, in the form of granules or pellets.

15 Contrary to what is specified in scientific and patent literature, the ZSM-12 material has the best catalytic performances at $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios < 200 (mol/mol). The best catalytic performances refer to both yields to propylene and stability (duration) of the catalyst over a period of 20 time.

The following examples are provided for a better understanding of the present invention.

EXAMPLES

25 The catalytic testing experiments were carried out in a continuous laboratory plant, with a fixed bed tubular re-

actor configuration. The reaction products were characterized with a gaschromatograph model HP 5890 equipped with a "PONA" capillary column.

5 The synthetic mixture of C₄ hydrocarbons indicated in Table 1 was used for the experimental tests. This mixture has a similar composition to the stream called "Refined III" deriving from steam cracking.

Table 1. Mixture used in the catalytic tests

Hydrocarbon	Feeding (weight %)
1-butene	/
Trans-2-butene	52.35
Cis-2-butene	24.86
n-butane	22.61
Iso-butane	0.18
Sum of olefins	77.21

20 The weight quantities of hydrogen, methane, ethane, ethylene, propane, propylene, n-butane, isobutane, 1-butene and isobutene, cis-2-butene, trans-2-butene, butadiene and a fraction of heavier products called C₅⁺, were determined in the gaseous reaction products.

25 The catalyst was charged in a quantity varying from 2

to 10 g, in granules of 20-40 mesh or in pellets of 2-4 mm, mixed with corindone (inert product), in a weight ratio of 1:1.

EXAMPLE 1. Synthesis of ZSM-12 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 100 \text{ mol/mol}$)

5 2.4 g of sodium aluminate with a content of Al_2O_3 equal to 56% are added to an aqueous solution of tetramethylammonium hydroxide at 35%. The solution thus obtained is poured, under stirring, into 200 g of colloidal silica Ludox HS 40.

10 A limpid, homogeneous gel is obtained, which is poured into an AISI316 steel autoclave, equipped with an anchor stirrer. The gel is left to crystallize under hydrothermal conditions at 165°C for 90 hours.

15 After cooling the autoclave, the solid obtained is separated from the mother liquor and washed with demineralized water until the washing water has a pH of less than 9.

The solid obtained is calcined at 550°C in a stream of air for 5 hours.

20 The solid thus obtained is subjected to ionic exchange by means of suspension in an aqueous solution of ammonium acetate. The ammonium ion is present in excess with respect to the nominal aluminum present in the solid. After filtration and washing of the solid, the whole operation (exchange and washing) is repeated.

25 The solid obtained is calcined at 550°C in a stream of

air for 5 hours.

The zeolitic solid is thus obtained in its acid form which, upon XRD analysis reveals the presence of the sole crystalline phase of the ZSM-12 type (MTW). Chemical 5 analysis shows a content of residual sodium of less than 50 ppm and a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$.

COMPARATIVE EXAMPLE 2. Synthesis of ZSM-12 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 250$ mol/mol)

0.97 g of sodium aluminate with a content of Al_2O_3 10 equal to 56% are added to an aqueous solution of tetramethylammonium hydroxide at 35%. The solution thus obtained is poured, under stirring, into 200 g of colloidal silica Ludox HS 40.

A limpid, homogeneous gel is obtained, which is poured 15 into an AISI316 steel autoclave, equipped with an anchor stirrer. The gel is left to crystallize under hydrothermal conditions at 165°C for 90 hours.

After cooling the autoclave, the solid obtained is separated from the mother liquor and washed with demineralized water until the washing water has a pH of less than 20 9.

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to the nominal aluminum present in the solid. After filtration and washing of the solid, the whole operation (exchange and washing) is repeated.

The solid obtained is calcined at 550°C in a stream of air for 5 hours.

The zeolitic solid is thus obtained in its acid form which, upon XRD analysis reveals the presence of the sole crystalline phase of the MTW type. Chemical analysis shows a content of residual sodium of less than 50 ppm and a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 250$.

EXAMPLE 3. Catalytic test with ZSM-12 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$ mol/mol)

The catalytic testing of ZSM-12 zeolite having a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$ (example 1), was carried out using the equipment described above and under the following operating conditions:

Reaction T = 500°C;

Total pressure = 1 bar;

WHSV_{total} = 1 h⁻¹;

Feeding = see Table 1.

The WHSV is defined as a ratio between the hourly weight flow-rate (g/h) of the mixture in the feeding divided by the weight of the catalyst (g). From a dimensional point of view it is h⁻¹.

Figure 1 indicates the two curves relating to total

conversion and selectivity to propylene, obtained with the catalyst ZSM-12 having a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$, in relation to the time on stream (tos).

The total conversion is defined as follows:

5 Tot. conv. % = [(C_4 at the reactor inlet) - (C_4 at the reactor outlet)] / (C_4 at the reactor inlet) • 100.

In this way the C_4 fraction is not divided into olefins or paraffins but is considered altogether as a potential reagent.

10 The selectivity to propylene is calculated as:

Selectivity to propylene % = (yield to propylene)/(total conversion) • 100.

The yield to propylene is experimentally obtained by gaschromatographic analysis.

15 In addition to the high conversion and selectivity values, the unexpected stability of this material over a period of time is extremely important. In fact, it can be noted from the graph of Figure 1 that no catalytic deterioration phenomena are present until at least 140 h of tos.

20 This stability over a period time makes the material particularly suitable for use in simple reactor conditions such as fixed beds.

More complicated solutions, however, such as fluidized/transported beds can obviously also be used.

25 Table 2 indicates, for illustrative purposes, the se-

lectivity of the different components forming the product at the outlet of the plant. Among olefins of interest, ethylene is also present (7.88%). C₅⁺ refers to the liquid fraction, at atmospheric pressure and room temperature, of the product leaving the plant. Owing to the high number of hydrocarbons present in the C₅⁺ fraction, Table 3 indicates the composition of this fraction subdivided by group of compounds. As the composition of the products depends on the operating conditions, Table 3 specifies two distributions obtained at two different reaction temperatures.

Table 2. Selectivity after 146 hours at a conversion of 55%

	Product	Selectivity (weight %)
15	Hydrogen	0.38
	Methane	0.8
	Ethylene	7.88
	Ethane	0.78
	Propylene	39.1
	Propane	5.54
	C ₅ ⁺	45.52
	Total	100.00

Table 3. Composition of the C₅⁺liquid fraction obtained
with ZSM-12 (SiO₂/Al₂O₃ = 100 mol/mol) in weight %

Reaction T (°C)	BTX %	NAPHTHALENES %	C ₅ ⁺ (non aromatics) %	OTHERS %
500	40	8	17.5	34.5
500	55	7	5.5	32.5

The term BTX refers to benzene, toluene and xylenes. The
10 heading NAPHTHALENES comprises all hydrocarbons, variously
substituted, of the naphthaline family. The term C₅⁺ (non
aromatics) refers to non aromatic hydrocarbons, saturated
and mono-unsaturated, containing 5-8 carbon atoms. The term
OTHERS comprises those products for which it was not possi-
15 ble to effect a gaschromatographic characterization

It can be seen how among the by-products, there are
large quantities of easily exploitable products such as
BTX.

COMPARATIVE EXAMPLE 4. ZSM-12 (SiO₂/Al₂O₃ = 250 mol/mol)

20 The catalytic testing of ZSM-12 zeolite having a molar
ratio SiO₂/Al₂O₃ = 250, whose synthesis is described in ex-
ample 2, was effected using the equipment described above
and under the exact operating conditions specified in exam-
ple 3.

25 Figure 2 indicates the two curves relating to total

conversion and selectivity to propylene, obtained with this zeolite in relation to the time on stream (tos). The conversion and selectivity to propylene are defined as in example 3.

5 Contrary to what is specified in literature, the catalytic performances of ZSM-12 with a ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 250$, are lower both in terms of yield (product of selectivity and conversion) and duration, with respect to the zeolite having a greater content of Al_2O_3 .

10 It can be observed, in fact, from the graph of Figure 2 how, already after 25 hours of tos, evident catalytic deterioration phenomena are present.

15 Table 5 indicates, for illustrative purposes, the selectivity of the various components forming the product at the plant outlet. Table 6, on the other hand, indicates the composition of the Cs^+ liquid fraction subdivided by group of compounds.

Table 5. Selectivity after 24 hours at a conversion of 52%

	Product	Selectivity (weight %)
5	Hydrogen	0.4
	Methane	0.6
	Ethylene	4.41
	Ethane	0.42
	Propylene	37.0
10	Propane	3.82
	C ₅ ⁺	53.35
	Total	100.00

Table 6. Composition in weight % of the C₅⁺ liquid fraction obtained with ZSM-12 (SiO₂/Al₂O₃ = 250 mol/mol)

	Reaction T (°C)	BTX %	NAPHTHALENES %	C ₅ ⁺ (non aromatics) %	OTHERS %
20	500	35	3.5	17.5	44

The term BTX refers to benzene, toluene and xylenes; the heading NAPHTHALENES comprises all hydrocarbons, variously substituted, of the naphthaline family; the term C₅⁺ (non aromatics) refers to non aromatic hydrocarbons, saturated and mono-unsaturated, containing 5-8 carbon atoms. The term

OTHERS comprises those products for which it was not possible to effect a gaschromatographic characterization.

COMPARATIVE EXAMPLE 5. Commercial ZSM-5

The catalytic testing of commercial ZSM-5 zeolite (CBV 5 3020 E) having a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$, was effected using the equipment described above and under the exact operating conditions described in example 3.

Figure 3 indicates the two curves relating to total conversion and selectivity to propylene, obtained with this 10 zeolite in relation to the time on stream (tos).

The conversion and selectivity to propylene are defined as in example 3.

The catalytic performances of ZSM-5 are much lower both in terms of yield (product of selectivity and conversion) and duration, with respect to the ZSM-12 zeolite. 15

It can be observed, in fact, from the graph of Figure 3 how, already after 10 hours of tos, evident catalytic deterioration phenomena are present.

Table 7 indicates, for illustrative purposes, the selectivity of the various components forming the product at 20 the plant outlet.

Table 8 specifies the composition of the C_5^+ fraction subdivided by group of compounds.

Table 7. Selectivity after 27 hours at a conversion of 85%

	Product	Selectivity (weight %)
5	Hydrogen	1.63
	Methane	3.70
	Ethylene	3.03
	Ethane	5.14
	Propylene	3.84
	Propane	34.15
	C ₅ ⁺	48.51
Total		100.00

Table 8. Composition in weight % of the C₅⁺ liquid fraction
15 obtained with commercial ZSM-5

	Reaction T (°C)	BTX %	NAPHTHALENES %	C ₅ ⁺ (non aromatics) %	OTHERS %
20	500	80	--	--	20